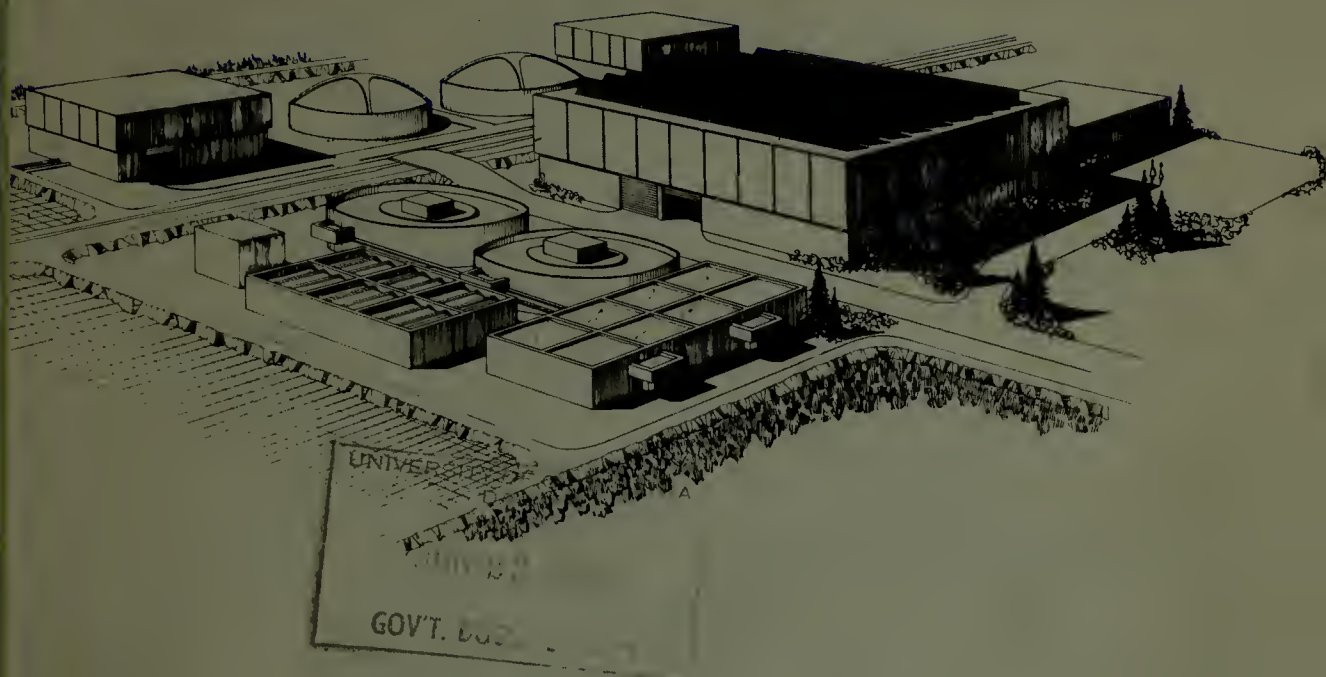


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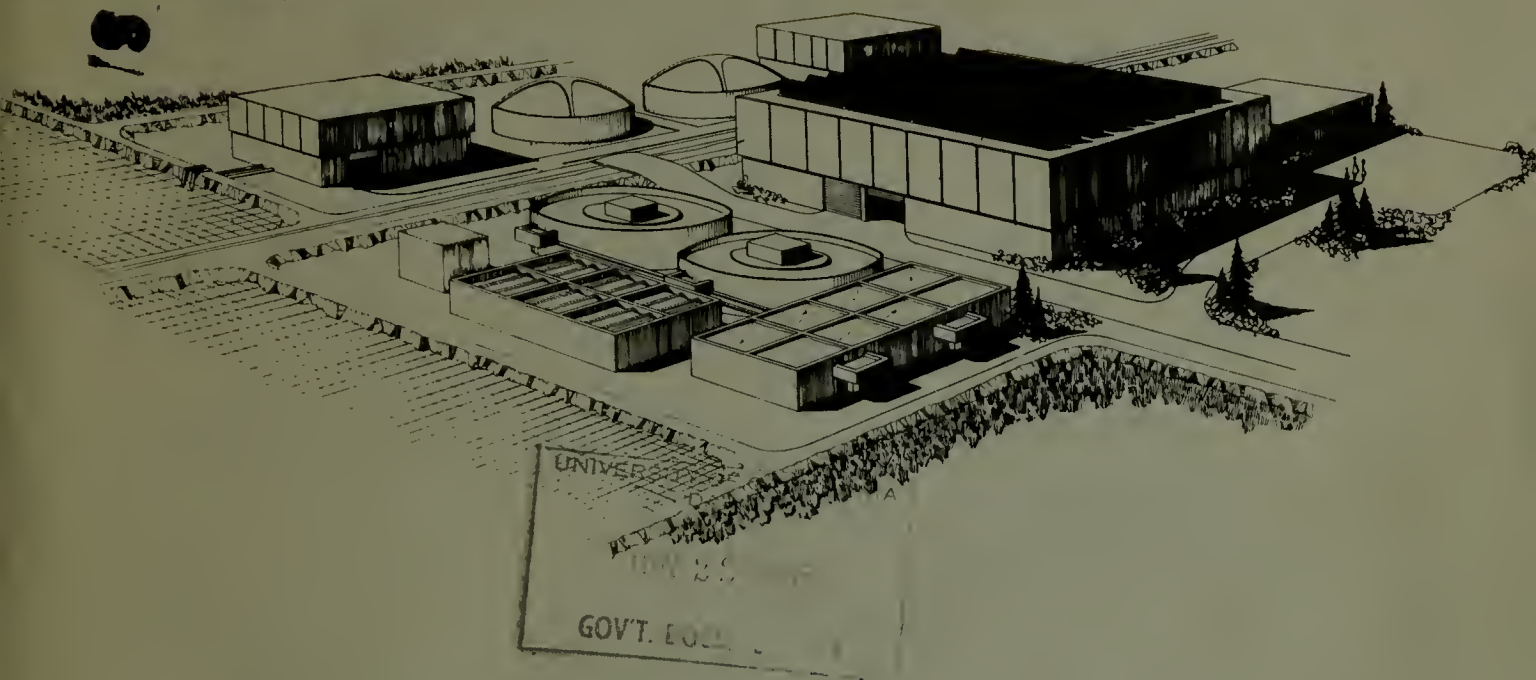
California
Resources Agency

Department of
Resources



Cultural Waste Water Desalination Reverse Osmosis

Report II



State of California
The Resources Agency

Department of
Water Resources



Agricultural Waste Water Desalination By Reverse Osmosis

Final Report Phase II

Bulletin 196-83
May 1983



ON THE COVER—Since the techniques for a successful desalting operation have been developed and tested at Firebaugh, a larger demonstration desalting facility is now under construction in Los Banos, California. This facility is the main component of DWR's project to demonstrate the feasibility of reclaiming agricultural drainage water to supplement State water supplies.

**Department of
Water Resources
Bulletin 196-83**

Agricultural Waste Water Desalination By Reverse Osmosis

Final Report Phase II

May 1983

Gordon K. Van Vleck
Secretary for Resources

George Deukmejian
Governor

Howard H. Eastin
Interim Director

**The Resources
Agency**

**State of
California**

**Department of
Water Resources**

FOREWORD

This report reviews the reverse osmosis (RO) pilot plant desalination studies conducted between 1976 and 1979 by the California Department of Water Resources (DWR) at the Waste Water Treatment Evaluation Facility near Firebaugh, California. This study was a continuation of the desalination activities that began in 1971 and were previously reported upon in DWR Bulletin 196-76.

The study used a tubular RO plant developed at the University of California, Los Angeles (UCLA), which was operated in cooperation with UCLA engineering staff. The plant was used to investigate various design and operating criteria that would be encountered in the large-scale desalination of brackish agricultural waste water by the RO process.

The RO plant successfully desalted brackish waste water at recovery levels exceeding 90 percent while supplying product water of acceptable quality. Softening pretreatment of feedwater with a model ion-exchange column, using RO waste brine as the resin regenerant, was successfully demonstrated. The use of brine from the RO system for the feedwater softening process offers an economical approach to scale prevention in the RO system without adding to the waste brine disposal load and reduces chemical requirements.

Once construction is completed in 1983, the plant will be operated over a period of three years to develop a full range of data on the desalting process to provide the basis upon which DWR will decide whether to build one or more full-scale desalting facilities.



Howard H. Eastin, Acting Director
Department of Water Resources
The Resources Agency
State of California

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The California Water Commission serves as a policy advisory body to the Director of Water Resources on all California water resources matters. The nine-member citizen commission provides a water resources forum for the people of the State, acts as liaison between the legislative and executive branches of State Government, and coordinates Federal, State, and local water resources efforts.

ACKNOWLEDGMENT

The use of the tubular reverse-osmosis plant was made possible through the cooperation of the engineering staff of the University of California, Los Angeles, including Professor Joseph W. McCutchan, Ed Selover, and graduate student Vinay Goel. The engineering staff also provided the means for installing and operating the membrane fabrication shop, and Mr. Selover designed much of and built the equipment.

The engineering staff of the University of California, Berkeley, including Professor Theodore Vermeulen, Gerhard Klein, and participating graduate students, provided the technical support for the model ion-exchange studies.

CHAPTER I. INTRODUCTION

This report reviews investigations made by the San Joaquin District of the California Department of Water Resources (DWR) on the desalination of subsurface tile drainage water between 1976 and 1979. The District conducted these investigations at the Waste Water Treatment Evaluation Facility (WWTEF), located along the Delta-Mendota Canal about 5 kilometres (3 miles) west of Firebaugh on 1.2 hectares (3 acres) of land.

Investigations at the WWTEF concerned the operation of a reverse-osmosis (RO) pilot plant and related desalination projects using this plant, including on-site fabrication of the tubular RO membrane and bench-scale ion-exchange (IX) studies that used RO brine for resin regeneration. The objective of these investigations was to establish the basic technical feasibility of desalting agricultural drainage water by reverse osmosis. No attempt was made to develop costs based upon this work.

The present RO desalting facility occupies a test shelter and membrane fabrication shop. The shelter is a 5.5-by-24-metre (18-by-80-foot) structure that houses a small office space and all RO test equipment. The membrane fabrication shop is housed in a remodeled laboratory. (This facility is described in detail in Chapter IV.) New desalting facilities are now under construction in Los Banos, about 48 km (30 mi) northwest of Firebaugh.

Background

The San Joaquin Valley is the southern half of the Great Central Valley of California. The Valley's drainage problems have been increasing in extent and severity in the last fifty years, and by the year 2000, almost 230 000 hectares (600,000 acres) will be affected unless drainage facilities are installed. Without drainage, agricultural productivity will be lost. The final result may be similar to what has happened in parts of the Middle East, where lands that once supported prosperous early civilizations are now salt deserts -- virtually useless. For this to happen here would be a tragedy, since the San Joaquin Valley is one of the world's most productive farming areas.

The drainage facilities needed to remedy the Valley's drainage problems are on-farm subsurface drainage systems, drainage collector systems, and a central disposal facility (the main obstacle impeding construction of on-farm and collector systems). On-farm systems are networks of buried, perforated pipes that drain excess water from the plant's root zone. The salty effluent from these pipes is collected in ditches and discharged to a central disposal facility that conveys drain water to a place where salt may be safely disposed.

Agricultural drainage facilities convey water, but the problem they control has more to do with salt. If water alone caused the drainage problem, it would be pumped out and reapplied for irrigation or allowed to remain in the ground for subirrigation. Salt, derived mainly from

natural weathering of the earth's crust, is the crux of the Valley's agricultural drainage problem, and water provides a medium for conveying salt out of agricultural areas. If it were feasible to separate salt from water and dispose of the salt only, this would be done, since water is a scarce and vital commodity in the San Joaquin Valley.

As early as 1967, DWR made various attempts to reclaim or improve the quality of agricultural waste water. During this time, DWR, as a member of an interagency study group that established the WWTEF (originally the Agricultural Waste Water Treatment Center) near Firebaugh, investigated various biological and chemical processes required to condition the waste water for disposal into a drainage system or estuarial waters. The Firebaugh location was ideal because of the year-round availability of agricultural waste water from the Alamosa tile drainage system.

DWR's first agricultural waste water desalination investigation was made in 1971, with the test operation of a tubular membrane RO pilot plant developed by the University of California, Los Angeles (UCLA). This plant was obtained for experimental purposes under a cooperative arrangement, whereby UCLA provided the equipment and technical support and DWR supplied the personnel and facilities at the WWTEF for operation of the RO plant. Test operations at this RO plant established the feasibility of desalting brackish tile drainage water by reverse osmosis and developed appropriate operating techniques and feedwater pretreatment procedures.

The first UCLA-designed equipment to be test-operated was a pilot plant consisting of 24 tubular assemblies. This plant was followed by a second desalting unit comprised of 180 tubes and a third, special-purpose, 60-tube unit designed to investigate the effects of feedwater treatment chemicals on the RO process.

Following the UCLA investigations, DWR and the U. S. Department of the Interior's Office of Water Research and Technology (OWRT) (formerly the Office of Saline Water) jointly sponsored a test program for evaluating three different membrane configurations of RO equipment to desalt subsurface tile drainage. The units had desalting capacities between 7 600 and 19 000 litres (2,000 and 5,000 gallons) per day and employed desalting modules of differing designs. OWRT supplied two types of membrane -- a hollow-fine-fiber design and a spiral-wound design -- and DWR supplied a tubular-membrane design obtained from UCLA.

DWR prepared the WWTEF facilities for the program, installed the equipment, and provided the personnel to operate the units. Funds for the program were jointly provided by DWR and OWRT. The program began in 1973 and lasted 18 months. The RO units were tested simultaneously, under similar operating conditions, using feedwater from the same source to provide a common basis for evaluation.

During the RO desalting studies, DWR contracted with the University of California, Berkeley (UCB), to study the effects of bacterial activity on the life and performance of the RO membranes. This bacteriological study was conducted concurrently with the RO studies at the WWTEF, and UCB investigators performed the necessary laboratory work in Berkeley. In the UCB study, bacterial organisms responsible for membrane

deterioration and surface fouling were identified, and the effectiveness of using several feedwater treatment chemicals as bactericides was evaluated.

Current Investigations

Between 1976 and 1979, work was directed toward improving equipment design, RO productivity, and feedwater treatment methods. A tube-type RO pilot plant, with additional tubes to expand its desalting capacity, was used for this development work. The plant had the same configuration as earlier tube-type pilot plants supplied by UCLA, plus several new operating features. Additionally, its tubular assembly could be easily fabricated and installed, which facilitated a variety of test operations, some involving membrane replacement.

Areas investigated using the tube-type plant were (1) the limits of product recovery based on the scaling threshold of calcium sulfate (CaSO_4) under different feedwater pretreatment conditions, (2) the combined membrane cleaning procedure and flow-reversal system designed to improve membrane productivity, and (3) the extent of silica solubility in RO brine when the brine was concentrated to high levels of total dissolved solids (TDS) content.

CHAPTER II. SUMMARY AND CONCLUSIONS

This chapter summarizes DWR's RO desalting activities. It also lists three conclusions that DWR reached after the RO activities were completed.

Summary

Investigations into the technical aspects of RO desalting (begun in 1971) were continued in 1976 as preparations were made for the installation of a large-capacity, tube-type RO pilot plant being fabricated at UCLA. This RO plant had a nominal desalting capacity of 95 000 litres (25,000 gallons) per day, and its 500 tubes were grouped into three racks composing a two-stage, parallel-series configuration. DWR started up the plant on April 27, 1976, and shakedown operation was completed in June 1976.

In July 1976, operating runs were conducted to obtain data on maximum product recovery using different feedwater pretreatment systems. The first series of runs used feedwater with either no treatment or treatment with sodium hexametaphosphate (SHMP). In succeeding runs, the RO plant was supplied with softened feedwater and operated at higher product recovery levels. These operations served to validate equipment design and provide data on plant performance and limits of product water recovery. Maximum product recovery was defined as the level of incipient scaling in the last tubes of the flow path where brine concentrations were highest.

A method of automatically cleaning the RO membranes was devised on the second-stage rack and tested to determine its effectiveness. The results indicated that this method was at least as effective as manual spongeball cleaning and did not affect the performance of the RO membrane adversely.

The RO plant was used to conduct a series of tests to examine the extent of silica solubility in RO reject brine. The silica contents of reject brine samples were used to establish a correlation between silica solubility, supersaturation, and precipitation loss. The results showed no evidence of precipitate formation but, rather, indicated the existence of silica in the supersaturated or colloidal state.

Ion-Exchange Studies

A bench-scale study was conducted at the WWTEF to investigate the use of RO brine for regenerating the IX softener in place of the conventional method of regeneration which uses sodium chloride (NaCl) salt. The initial period of operation with the bench-scale model dealt with problems of CaSO_4 precipitation in the IX column and degradation of resin exchange capacity. Considerable attention was given to salvaging and renovating the resin as a result of precipitate formation. Eventually, researchers developed an operating procedure for resin regeneration with use of a blend of previously used and fresh RO brine and upflow regeneration through the IX column. This procedure proved successful in preventing accumulation of CaSO_4 solids in the column and maintaining the life of the resin.

Other Reverse-Osmosis Activities

Throughout 1977, the RO plant was operated to supply product and brine waters for other activities at the WWTEF, and product water recovery was as high as 90 percent. Between May 1977 and August 1978, a silica solubility study and flow-reversal tests were run at the RO plant. Between August and November 1978, the 500-tube plant was reequipped with new membranes, and from February to August 1979, a system optimization study was conducted at the plant in cooperation with UCLA. DWR personnel operated the equipment, collected the data, and forwarded their findings to UCLA for analysis. Data obtained from the studies were used to develop a computer program that provided an optimization model of the 500-tube RO plant.

Membrane Fabrication

A membrane fabrication laboratory was established at the WWTEF to equip the RO plant with its initial 500 tubes and supply all replacement needs. The fabrication procedure used at the laboratory was patterned after the methods and equipment developed by UCLA for making the cellulose acetate (CA) membrane. The membranes were fabricated by site personnel assigned to operate the RO plant.

The laboratory demonstrated that manufacturing CA membranes was a relatively simple process, requiring the use of only semiskilled labor and off-shelf equipment. Since membranes were easy to replace, high-risk operations such as the scaling threshold and silica studies could be performed with the tube-type RO plant.

See appendix for details of membrane fabrication at the WWTEF.

Conclusions

The following conclusions are based on the results of the various RO studies conducted by DWR during this period of operation.

1. Test runs on the 500-tube RO plant demonstrated that maximum product recovery was limited by CaSO_4 scaling on the RO membranes when desalting untreated feedwater or that treated with sodium hexametaphosphate. When desalting softened feedwater, maximum product recovery was limited primarily by equipment capability. The RO plant developed unstable operating conditions at recovery levels of about 95 percent because of low brine flow rates and extremely high brine concentrations. Further investigations should be made into resolving the instability condition, possibly by employing a booster pump to recirculate the brine through the RO tubes.
2. The flow-reversal procedure should be investigated as a means for reducing the instability condition caused by the low brine flow and high brine concentration at very high recovery operation.
3. The bench-scale IX tests indicated that RO brine TDS content ranging from 50 000 to 60 000 milligrams per litre was most suitable for

regeneration of IX resins. Also, the effectiveness of calcium (Ca) removal from the feedwater by ion-exchange was reduced considerably because of the large amount of magnesium (Mg) present in the feedwater. The regeneration with RO process brine was shown to be technically feasible, offering an acceptable alternative to the conventional method of resin regeneration. This process should be investigated further to determine its sustainability in a closed loop, RO, IX softening system and to determine its economic feasibility.

CHAPTER III. FEEDWATER SUPPLY, QUALITY, AND PRETREATMENT

Waste water for WWTEF tests was obtained from the Alamitos tile drainage system and pumped to a 3.1-million-litre (820,000-gallon) elevated storage pond. The tile drainage system serviced 162 hectares (400 acres) of farmland adjoining the desalting facility. The farmland was planted with field crops typically grown in that locality, including cotton, grain, and hay.

Flow from the tile drainage system varied throughout the year, with low flows occurring during the winter months and high flows in the summer months when the farmland was heavily irrigated. The TDS content of this water varied from 2 000 to more than 6 000 milligrams per litre, depending upon the season and the irrigation practice. Water drawn from the storage pond was essentially clear, with a pH of about 7.1, and water temperature varied seasonally from 13 degrees Celsius (55 degrees Fahrenheit) to 26° C (78° F). This water had an unusually high sulfate ion content, contributing to about one-half of the TDS content.

Table 1 compares the range of ionic constituents in the tile drainage water during periods of extreme high and low salinity. The composition of the feedwater at Alamitos varies according to the time of year (high TDS in winter, low in summer) and the type of crop being grown in the fields from which drainage occurs. The lowest summer TDS concentrations generally result from a rice crop or temporarily following irrigation of other crops (as was the case on July 20, 1976). The average composition of the Alamitos feedwater is typical of the 1981 average shown in Table 1.

TABLE 1
AGRICULTURAL DRAINAGE WATER QUALITY
(in milligrams per litre
unless otherwise noted)

Constituent	Low TDS 7-20-76	High TDS 3-23-78	1981 Average	San Luis Drain at Los Banos 4-14-82
Calcium	164	520	350	474
Magnesium	52	174	150	244
Sodium	402	1 500	1 002	2 220
Potassium	4.0	5.3	3.4	6.6
Bicarbonate	331	185	175	112
Sulfate	888	3 880	2 670	4 690
Chloride	203	655	424	1 360
Nitrate	16	80	--	177
Boron	4.1	13	10.3	14
Silica (SiO ₂)	25	45	42	21
Hardness (CaCO ₃)	625	2 010	1 530	2 190
TDS	1 930	7 230	5 120	9 440
EC (micromhos per centimetre)	2 670	8 030	5 900	11 300

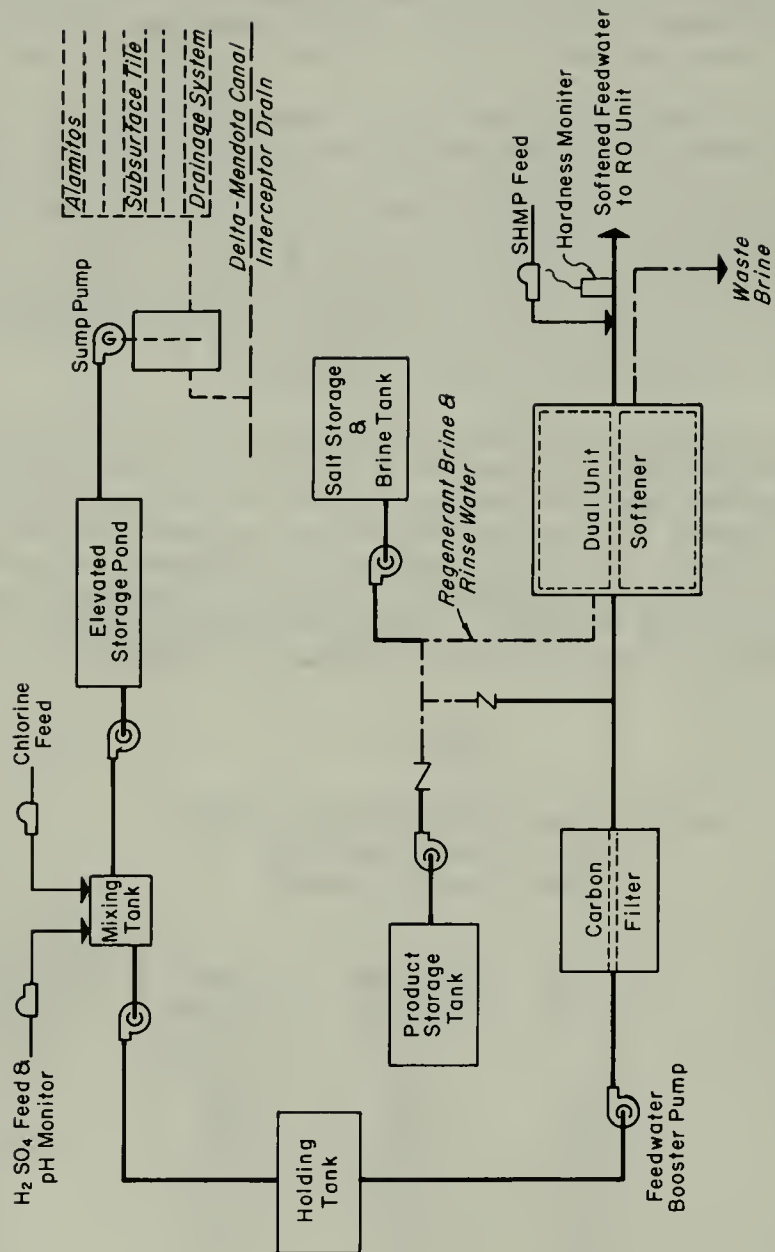


Figure 1. Flow Diagram - Feedwater Supply and Treatment Arrangement

Table 1 also analyzes drain water in the federal San Luis Drain, which is the source of feedwater for the Los Banos Demonstration Desalting Facility. This water quality is considered typical for areas of relatively new drainage systems such as Westlands Water District, which discharges into the San Luis Drain. Future large-capacity drainage water desalting plants in the San Joaquin Valley will have to be designed to handle variable water qualities. Currently, the valleywide drainage water TDS average is similar to that at Alamitos. As the installation of agricultural drains accelerates, however, average drainage water composition will be high until the effects of leaching salts eventually reduce salt concentrations in the soils to a level similar to Alamitos, which has been operating for about thirty years.

Figure 1 is a flow diagram of the feedwater supply and treatment arrangement used at the WTEF during the RO studies. The Alamitos tile drainage water was drawn from the storage pond and treated with three chemicals before the desalting process: concentrated sulfuric acid (H_2SO_4) to maintain a feedwater pH between 5.5 and 6.5, lithium hypochlorite to provide chlorine, and SHMP to inhibit scaling.

The feedwater was kept in a holding tank for about 40 minutes to allow for chlorine disinfection. It was then dechlorinated with activated carbon prior to IX softening. The feedwater booster pump provided the necessary pressure of about 275 kilopascals (40 pounds per square inch) to allow feedwater to flow through the system, supplying water to the RO plant.

The activated carbon filter was a dual unit with a capacity of 106 litres (28 gallons) per minute with both carbon columns operating. The water softener was a duplex unit with 114-L/min (30-gpm) processing capacity, designed to provide continuous feedwater deionization. Each column contained 0.85 cubic metre (30 cubic feet) of the polystyrene-DVB-sulfonate cation-exchange resin, which removed the hardness constituents (Mg and Ca) from the feedwater. Saturated NaCl brine was used for resin regeneration during operation of the 95 000-L/day (25,000-gpd) pilot plant, and a Hach hardness monitor was used to monitor the feedwater stream leaving the softener. To prevent $CaSO_4$ scaling in the RO tubes and possible damage in the event of a softener malfunction, the Hach monitor shut down RO operations when it detected total hardness levels exceeding 100 mg/L. Additionally, a pH analyzer controlled the chemical feed pump operation to maintain the proper feedwater pH.

CHAPTER IV. THE 500-TUBE REVERSE-OSMOSIS PILOT PLANT

In June 1975, DWR began preparations to operate a larger capacity RO pilot plant to further define the design and operating criteria of agricultural waste water desalting. The tube-type RO unit developed by UCLA was selected for this plant. This unit had the same basic configuration and mechanical components as the smaller UCLA units operated at the WWTEF but contained 320 more tubes because of the larger capacity requirement. UCLA technicians designed and fabricated the plant and supervised its installation and startup at the WWTEF.

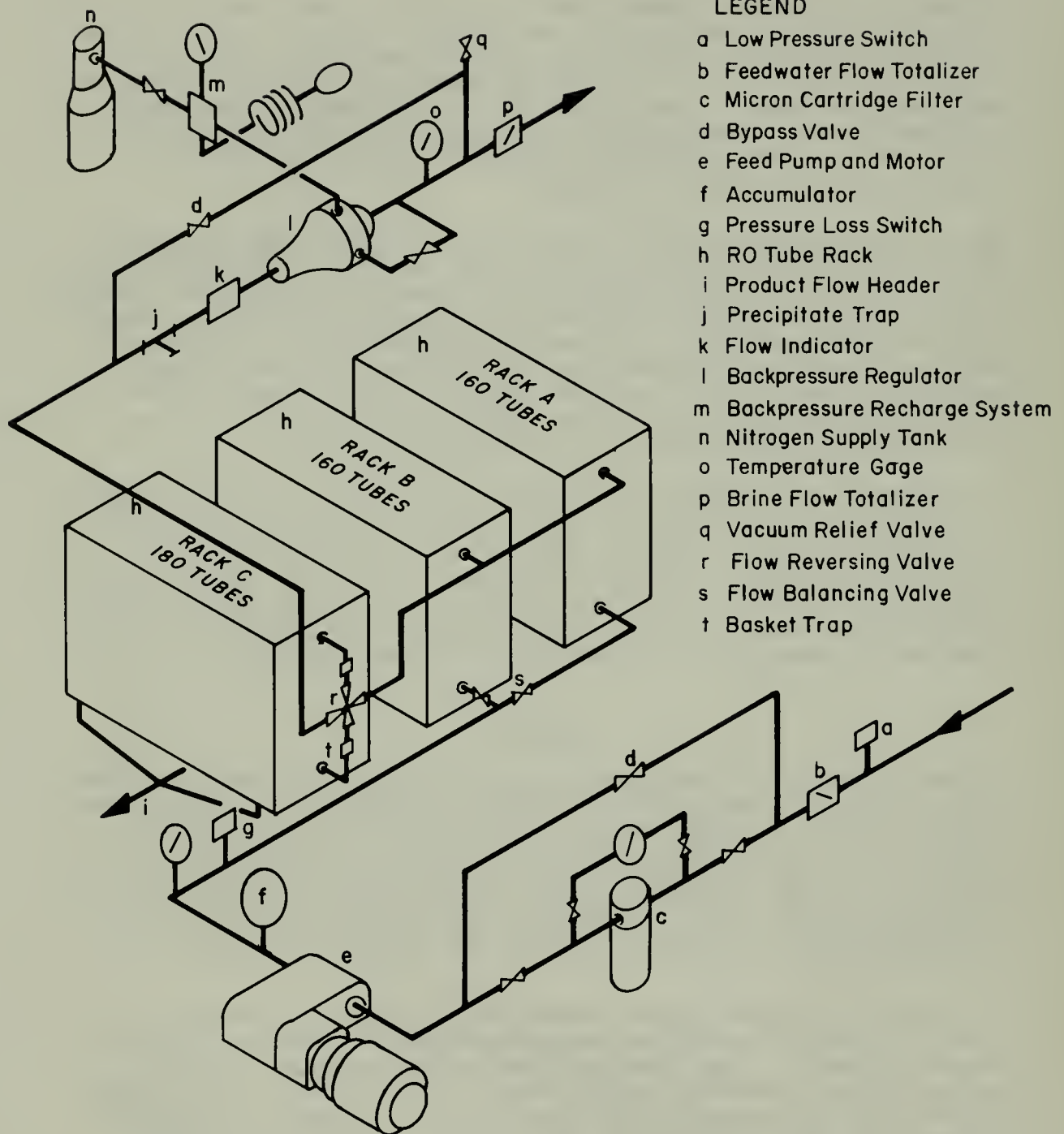
The 500-tube version of the RO pilot plant had a total membrane area of 104 square metres (1,120 square feet). The tubes were grouped into three racks to form a two-stage, parallel-series flow configuration as shown on Figure 2. The first stage consisted of two parallel racks (Racks A and B), each containing 160 tubes. Each rack was equipped with a flow control valve to balance the feedwater flow into the branches. The single, second-stage rack (Rack C) contained 180 tubes and followed in series with the first-stage racks. The membranes used in the earlier pilot plant operations were retained in the tubes of this rack.

To accommodate the larger flow requirement of the RO plant, the pistons of the triplex pump were enlarged from a 31.8-millimetre (1.25-inch) diameter to a 44.4-mm (1.75-in) diameter, thereby increasing pumping capacity. Additionally, individual plastic sleeves were placed over the RO tube to collect product water, thereby eliminating the corrugated plastic collection sheet previously used at smaller capacity, tube-type RO pilot plants. These design changes were made by the UCLA engineering staff.

Startup

The 500-tube RO pilot plant began shakedown operations on April 27, 1976, to test equipment components and establish criteria for obtaining maximum product recovery. Maximum recovery was indicated when scaling developed in the tubes. The extent of scaling was determined by passing the spongeball through the tubes of Rack C and observing the material flushed out with the brine. Rack C was observed because the brine concentration was highest there, and scaling occurred most frequently in the last few tubes of the rack.

Trial runs for maximum recovery began with the system pressure set at 2 760 kPa (400 psi), with flow reversal provided for the last rack at two-hour intervals. The feedwater flow rate was adjusted to attain maximum recovery, which was established by first setting a target brine salinity and then inspecting the tubes for scaling when the target was reached. The brine salinity was then raised or lowered by adjusting the feedwater flow according to the extent of scaling found in the tubes, with maximum recovery being established at the point of incipient scaling. Target brine salinities of 9 000 to 11 000 mg/L were reached during the desalting of untreated feedwater. During this period, the triplex pump experienced water leakage through its piston seals, and all of the tube membranes of Rack C were replaced with those prepared at the WWTEF.



Schematic Arrangement of 500-Tube (UCLA) RO Unit

Maximum Product Recovery

In July, after shakedown operations were concluded, the RO plant was operated in a series of runs using different feedwater pretreatment systems with the objective of obtaining maximum product recovery levels in conjunction with flow reversal.

During July and August 1976, operating runs were made using feedwater with no treatment or treatment with SHMP at dosages of 5, 10, and 20 mg/L. Operating data were recorded and are summarized on Figure 3. In these runs, the feedwater TDS ranged from 3 000 to 4 500 mg/L, and brine TDS ranged from 11 000 to 26 000 mg/L, depending upon the plant's operating recovery level. Feedwater flow rates ranged from 41.6 L/min (11 gpm) at the higher recovery levels to 75.7 L/min (20 gpm) at the lower levels. Product recovery was below 70 percent with untreated feedwater but as high as 90 percent with SHMP added to the feedwater.

During these runs, the flow reverser was not used in the usual automatic mode, but the flow was reversed periodically in Rack C. For each test run, the brine TDS was increased until scaling occurred; the plant was then shut down and the tubes were cleaned with a spongeball to determine the extent of scaling. Tube and equipment failure was minimal, except for occasional clogging of the pressure regulator and brine screen with CaSO_4 precipitate and malfunctioning of the triplex pump.

Maximum Recovery with Softened Feedwater

In September and October 1976, the plant was operated at higher pressure and recovery levels, using softened feedwater. All tubes were regularly cleaned with a spongeball, and water flow was periodically reversed in Rack C. Equipment outage and tube failure were more frequent because of increased stress from the plant's high operating pressure. Breakdown of the softener unit caused numerous outages and finally required a complete overhaul of the unit's main components.

Plant performance was determined by observing brine TDS and flow, since these parameters limited operation at higher recovery levels. Initial operating runs produced RO brine with a TDS of 29 000 mg/L, while final runs produced brine with a TDS of 80 000 mg/L at a flow rate of 1.5 L/min (0.4 gpm).

Attempts were made to operate the RO plant at levels producing brine with a TDS of 90 000 mg/L. However, plant operation at these levels proved unstable because a steady-state equilibrium could not be held between the feed flow and brine flow. Because of the extremely low brine flow rate, insufficient turbulence was created in the tubes. This condition adversely affected membrane permeability and resulted in abrupt fluctuations of brine flow that could not be prevented by adjusting the feed flow rate.

A series of runs was made in early November 1976 at operating pressures of 5 170 and 5 860 kPa (750 and 850 psi). Recorded data are summarized on Figures 4 and 5. Total ion rejection and product water recovery were 94.5 and 92.5 percent, respectively, for the 5 170-kPa (750-psi) run.

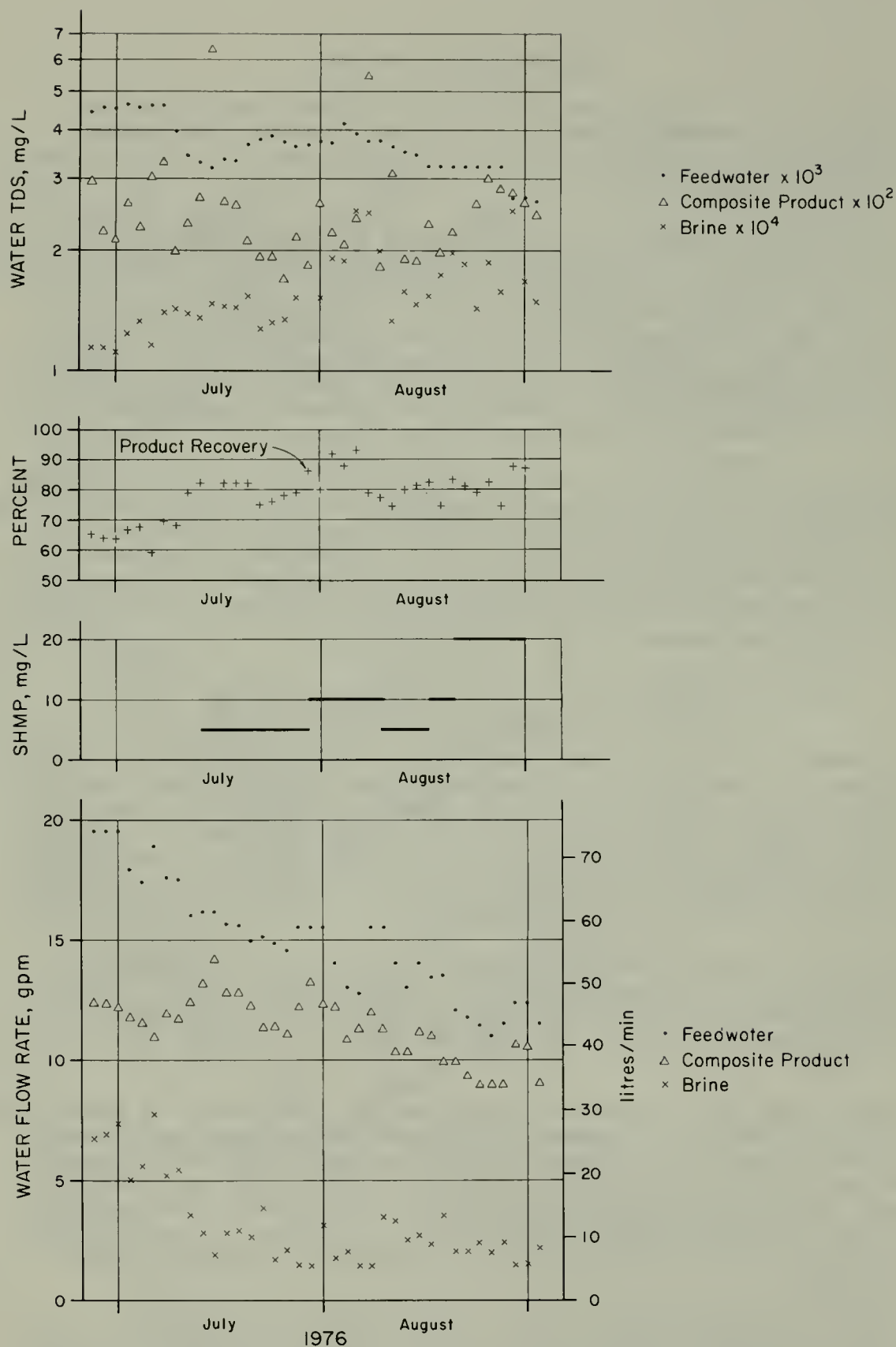


FIGURE 3. MAXIMUM PRODUCT RECOVERY WITH SHMP-TREATED FEEDWATER

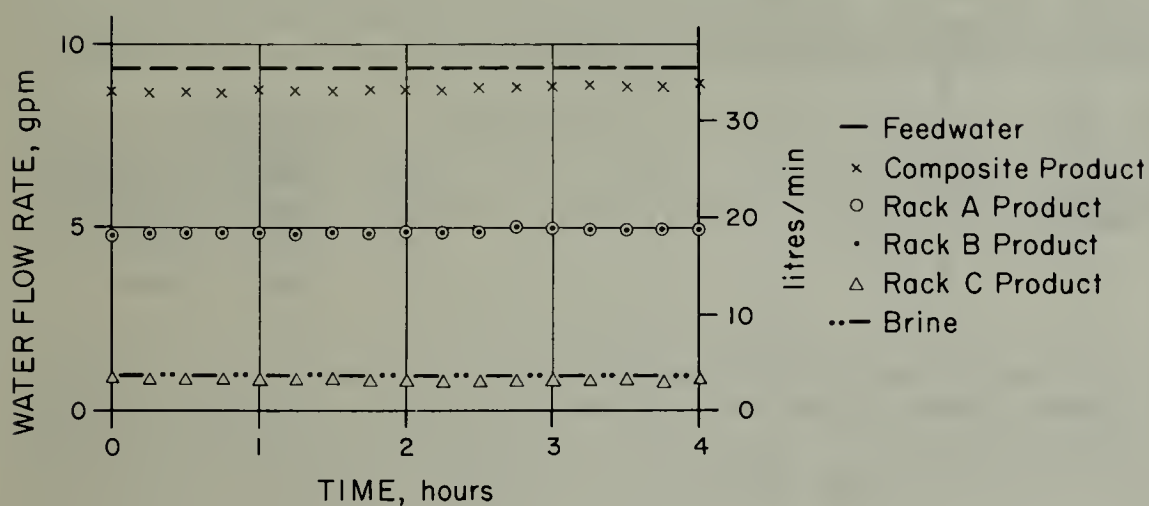
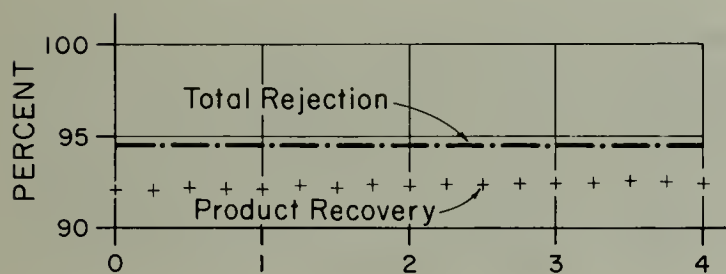
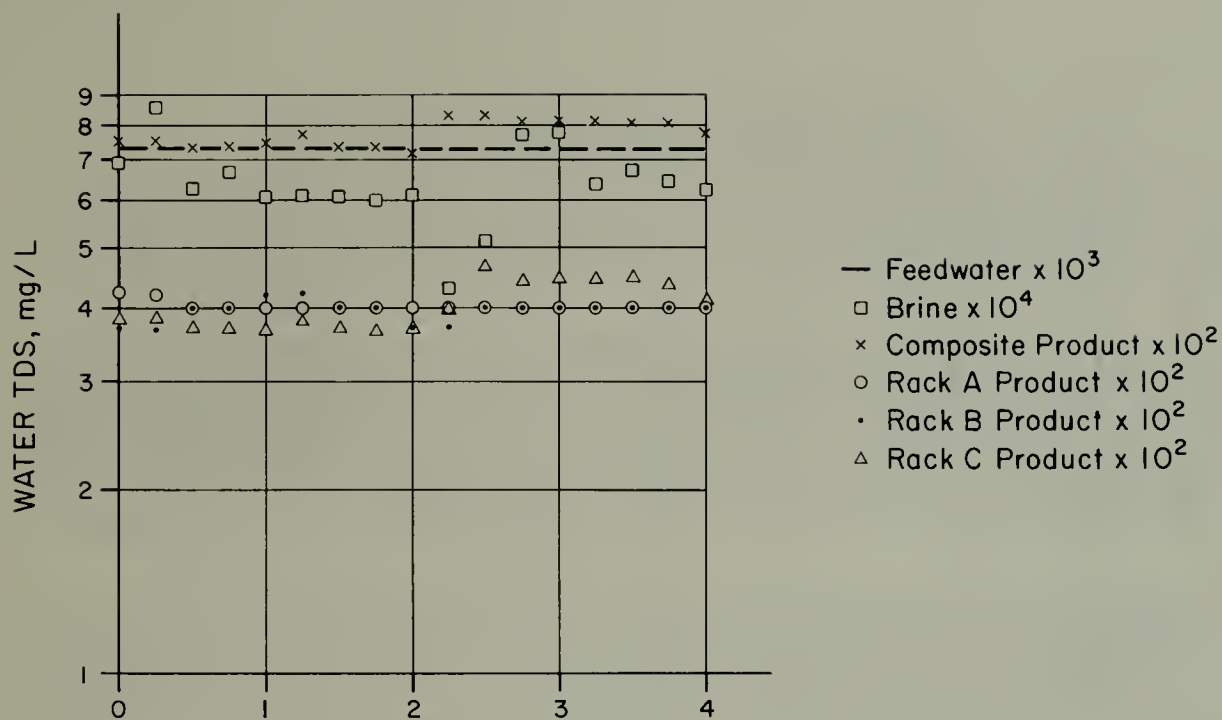


Figure 4. Maximum Recovery with Softened Feedwater
at 5170 kPa (750 psi)

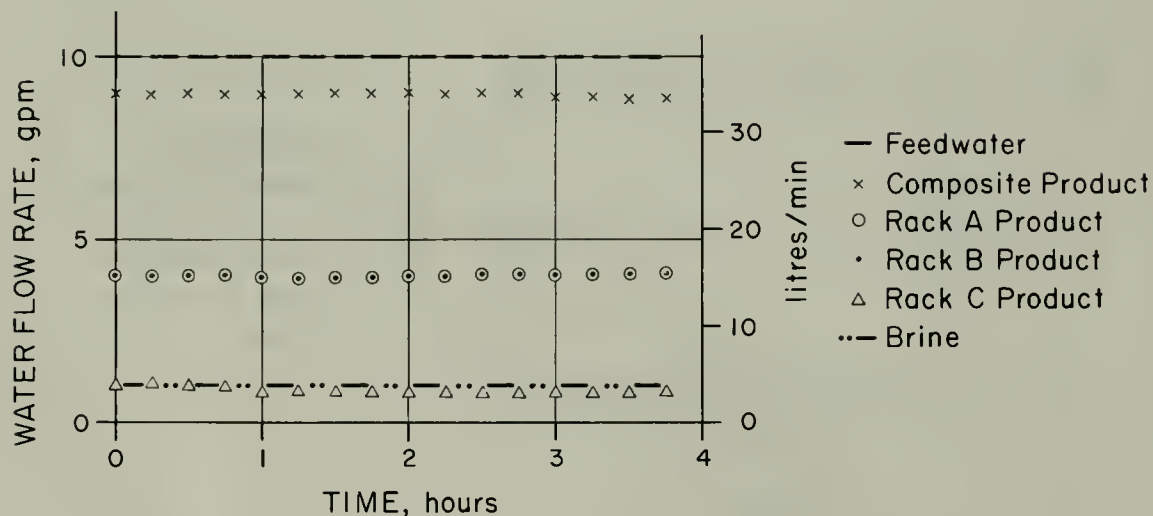
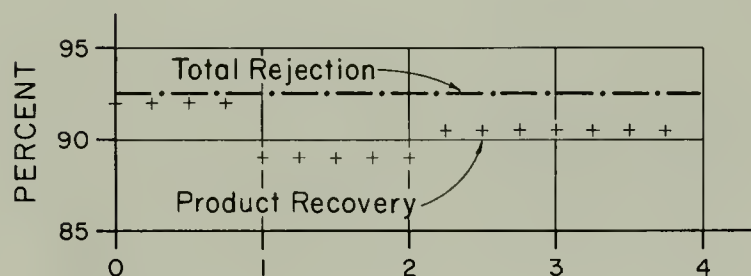
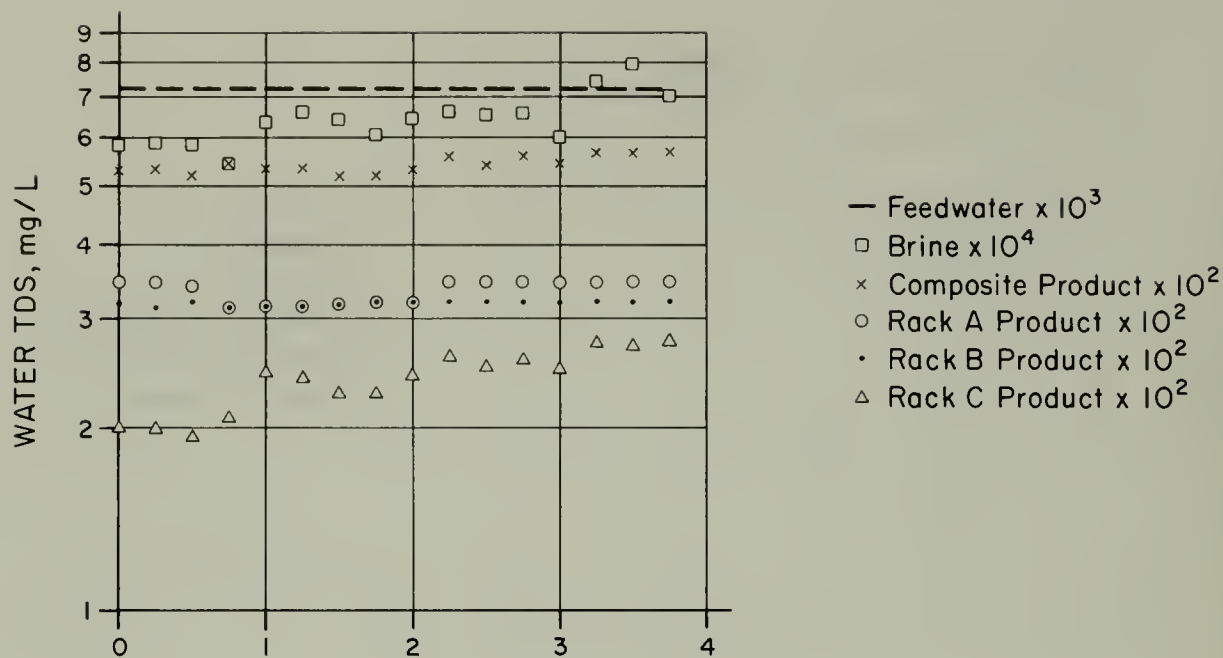


Figure 5. Maximum Recovery with Softened Feedwater
at 5860 kPa (850 psi)

Cyclical Cleaning of Reverse-Osmosis Tubes

An unusual feature of this RO plant was the use of an automatic, pneumatically controlled, flow-reversing valve. This flow-reversal concept, using the tube-type RO plant, was developed by UCLA in a study conducted at the LaVerne facility of The Metropolitan Water District of Southern California.

Flow reversal serves to reduce membrane fouling by producing periodic turbulence in the last tubes in a rack where the flow is low. It also improves maximum product recovery limited by CaSO_4 scale formation. Scaling takes place initially in the end tubes of the RO rack where the brine is most concentrated. The reversing valve is located on the second-stage rack where the brine concentration is relatively high and where the flow-reversing action is most effective.

A pair of basket traps was installed on the second-stage rack in February 1977, and a study was performed to evaluate the adequacy of the automated spongeball cleaning procedure. One basket trap held a spongeball that passed through the RO tubes to the other trap with each flow reversal. Three test runs were made during February and March 1977. The first two runs used the automatic cleaning service; the third run did not. A single spongeball was used for the test operation.

The RO plant was operated within a prescribed range of feedwater flow and pressure to provide a uniform level of product water recovery. The feedwater TDS did not fluctuate significantly during this time. Feedwater treatment consisted of acidification to a pH of 5.5 and chlorination, followed by dechlorination with an activated carbon filter. The feedwater was not softened but was treated with SHMP, which was added during the second and third tests on the first day of the first test run. The feedwater was passed through a 5-micrometre particulate filter before entering the RO plant.

Test data were recorded daily and are summarized in Table 2. No significant operating problems developed during the test period. After each test run, the plant was shut down and the three racks were cleaned manually with the spongeball to check the effectiveness of the automated cleaning procedure.

No significant amount of fouling matter was removed from any of the racks by manual spongeball cleaning. Test results indicate that the automatic spongeball cleaning procedure is at least as effective as manual spongeball cleaning and does not adversely affect the performance of the RO membrane.

Silica Solubility Tests^{1/}

A series of tests was conducted in 1977 and 1978 to examine the extent of silica solubility in RO brine. In these tests the RO plant was operated at recovery levels that produced waste brine with a TDS content ranging from 16 000 to 41 000 mg/L. Researchers analyzed the silica content of reject brine samples to establish a correlation between silica solubility, supersaturation, and precipitation loss.

^{1/} California Department of Water Resources Agricultural Waste Water Desalination Report No. 14, "Silica Solubility Tests", May 1979.

TABLE 2

SUMMARY OF SPONGEBALL CLEANING TESTS

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
Date (1977)	2-14 to 2-18	2-28 to 3-3	3-4 to 3-10
Days of operation	5	4	7
Reverse-osmosis plant			
Operating pressure (kPa)	4 480 to 4 550	4 450	4 450 to 4 585
Operating pressure (psi)	650 to 660	660	660 to 665
Flow rate (L/min)	59 to 60	61.7 to 64.0	61.7 to 62.1
Flow rate (gpm)	15.7 to 15.8	16.3 to 16.9	16.3 to 16.4
Feedwater			
TDS (mg/L)	5 200 to 5 500	5 200 to 5 300	5 250 to 5 300
Treatment	SHMP*	SHMP	SHMP
Product water (second-stage rack)			
Flow rate (L/min)	4.54 to 4.92	4.92 to 5.29	4.92 to 5.29
Flow rate (gpm)	1.2 to 1.3	1.3 to 1.4	1.3 to 1.4
TDS (mg/L)	625 to 850	756 to 1 000	600 to 725
Composite waste brine			
Flow rate (L/min)	20.4 to 21.9	26.1 to 28.0	26.1 to 27.6
Flow rate (gpm)	5.4 to 5.8	6.9 to 7.4	6.9 to 7.3
TDS (mg/L)	12 000 to 14 000	11 250 to 12 000	11 750 to 12 750
Overall plant recovery (percent)	57 to 66	56 to 58	56 to 58
Flow reversal	2-hour interval	2-hour interval	2-hour interval
Automatic spongeball cleaning	2-hour interval	2-hour interval	none
Manual spongeball cleaning (all racks)			
Date (1977)	2-21	3-3	3-10
Results	No fouling evidence	No fouling evidence	No fouling evidence

*On first day only.

DuPont literature^{2/} on the subject of silica solubility, pertaining to its B-9 Permasep permeator, served as a guideline for analyzing the test results of this study. This literature states that the ionic strength of the solution does not materially affect silica solubility, and when a saturated silica solution is concentrated, it becomes supersaturated. Also, in the absence of Ca, the silica can polymerize (develop molecular compounds) and form colloidal silica.

The highest TDS level of RO reject brine analyzed (40 000 mg/L) contained 140 mg/L of silica as silicon dioxide (SiO_2). There were no observed indications of precipitate formation at this or any lower level of brine TDS analyzed in the tests. By applying methods suggested in the DuPont literature when desalting Alamitos drainage water, it was determined that the solubility of silica in RO brine of 40 000 mg/L TDS exceeded that found in pure water but was below that tolerated in the B-9 permeator.

The softening process considerably reduced the Ca content in the reject brine, and it was determined that its cation constituent consisted mostly of Na ions.

In view of the cited literature and in the absence of precipitation formation, it was concluded that the silica in the reject brine existed in the supersaturated or colloidal state, most likely as sodium silicate, because of the high concentration of Na in the reject brine.

^{2/} DuPont Technical Bulletin 421, "Silica Solubility", March 1976.

CHAPTER V. ION-EXCHANGE STUDIES

An IX, bench-scale study was conducted concurrently with the silica solubility study and the flow reversal tests at the WWTEF. The study was based on earlier work by UCB on IX softening of sea water.^{1/} Later experiments conducted at the WWTEF used cooling water blowdown (concentrated saline solution that comes out of the bottom of cooling towers) as brine for IX resin regeneration to demonstrate the viability of the process.^{2/} The study at the WWTEF was conducted by DWR personnel, with technical support provided by UCB.

Resin regeneration with RO brine is intended to replace the conventional mode of regeneration using NaCl salt. The conventional method presents no technical problems, but the large salt requirement makes softening of agricultural waste water quite costly, and the NaCl salt becomes an added burden to the waste disposal load. Problems inherent with RO brine regeneration, such as low efficiency, gradual degradation of exchange capacity, and tendency for CaSO_4 precipitation in the IX column (resin bed), were encountered during the study.

The bench-scale IX column consisted of a clear plastic tube, 100 mm (4 in) in diameter by 1 520 mm (60 in) in length, filled to a depth of 500 mm (20 in) with a polystyrene-DVB-sulfonate cation-exchange resin. Plumbing and control devices provided alternate upflow or downflow operation through the column. DWR personnel designed and fabricated the test model.

In the first period of study (1975), DWR personnel worked to resolve the effects of CaSO_4 precipitation in the column and degradation of resin exchange capacity. While the softening mode was downflow through the column, both upflow and downflow modes were employed to regenerate the resin. Alamitos tile drainage water was used for feedwater, and waste brine from the 500-tube RO plant provided the regenerant brine.

DWR studied ways to salvage and renovate the resin from the effects of precipitate formation. Devices were altered or added to the system in attempts to remove the precipitate formed in the IX column. Hydrochloric acid or NaCl solution was applied to recondition the resin after heavy precipitation in the column or repeated regeneration with RO brine. In time, resin regeneration -- with a blend of used and fresh RO brine operating in the upflow mode -- minimized the effects of precipitation.

1/ Industrial and Engineering Chemistry Process Design and Development, "Ion-Exchange Equilibrium Data in the Design of a Cyclic Seawater Softening Process", Volume 3, page 280, July 1964.

2/ California Department of Water Resources and University of California Seawater Conversion Laboratory, "Agricultural Waste Water for Power Plant Cooling, Development, and Testing of Treatment Processes", Volume II, June 1978.

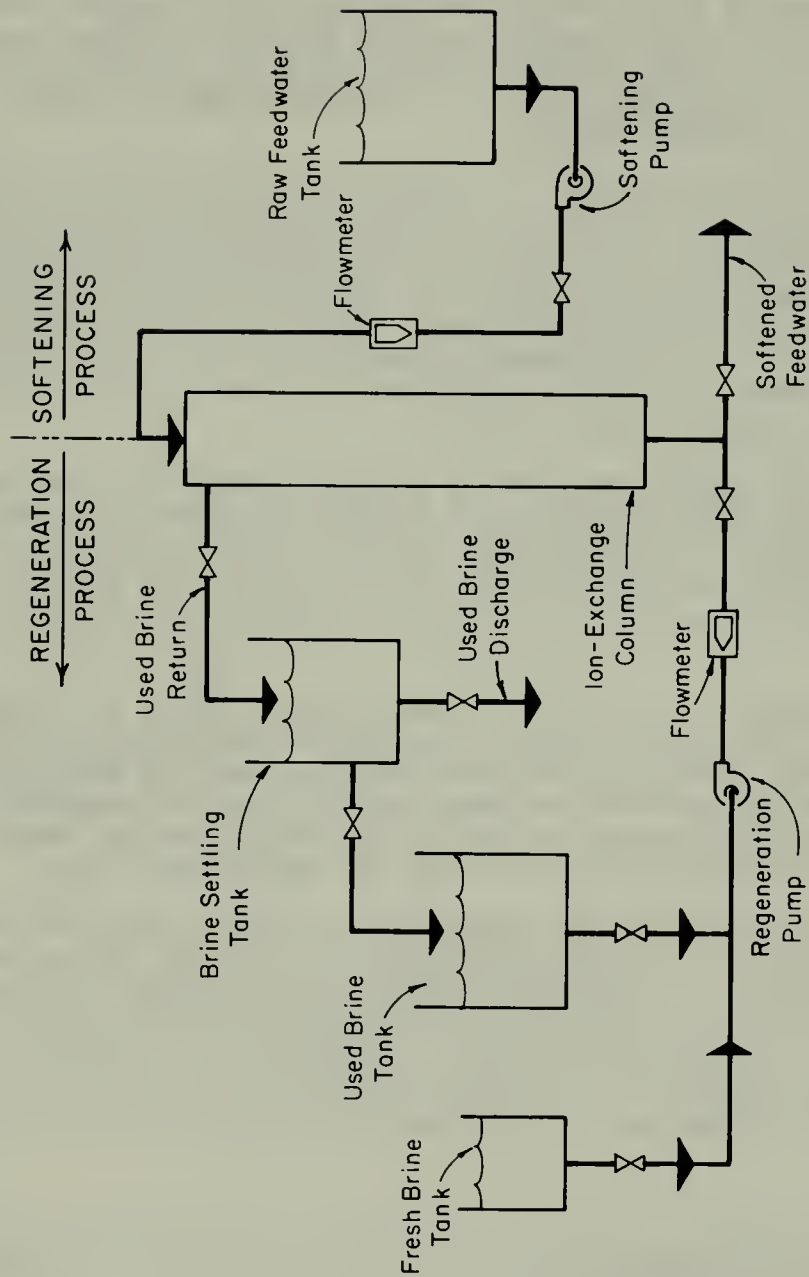


Figure 6. Ion-Exchange Model, Equipment and Process Arrangement

The second period of study (1977) was not fraught with the same problems encountered during the first period. Test runs successfully softened feedwater ranging from 2 700 to 6 000 mg/L TDS, using regenerant RO brine from 45 000 to 70 000 mg/L TDS. A single IX softening and regeneration cycle was normally completed during a working day. A schematic arrangement of the equipment and process is shown on Figure 6.

The softening step was performed in the conventional downflow mode at a flow rate through the column of about 1.7 L/min (0.44 gpm or 5 gpm/ft²) of column area. The Ca content of the effluent was monitored by periodic sampling, and the breakthrough point of the softening step was indicated when a substantial increase in the Ca concentration (20 mg/L) was observed. The volume of water softened and its composite Ca concentration were noted.

Regenerant brine was passed through the column at a rate of 3.3 L/min (0.88 gpm or 10 gpm/ft²) of column area. Upflow regeneration through the column was required to expand the resin bed to about twice its original height. This flow rate was sufficient to both separate the relatively small CaSO₄ crystals formed between resin beads in the resin bed by the regeneration reaction and carry the crystals up and out of the column but insufficient to carry out the larger resin beads. In addition, precipitation of CaSO₄ in the resin bed results in a lower concentration of Ca ions in the regenerating solution, which has the beneficial effect of driving regeneration toward completion.

A constant volume of blended RO brine was used in each regeneration step. For each regeneration, 76 litres (20 gallons) of used brine held from the previous regeneration run was first passed through the column. The first 9.5 litres (2.5 gallons) of this volume to pass through was discarded, while the remainder was returned to the settling tank. Next, 9.5 litres (2.5 gallons) of fresh brine was passed through the column and added to the used brine held in the settling tank. This 76-litre (20-gallon) quantity was then available for the next regeneration run. The combination of using the blended brine mixture and the upflow regeneration through the column to provide an expanded bed successfully eliminated CaSO₄ precipitation in the bed and maintained the life of the resin.

Four series of test runs were made, each using regenerant brine at different TDS levels. The number of completed runs made for each series and their respective regenerant TDS levels are given in Table 3. All quantitative analyses were made using the appropriate titration method (Hach kit). TDS was measured with a conductivity meter.

Table 3 provides test data for typical low and high feedwater TDS conditions found in each series of runs. Also included are calculated percentages of both the Ca removed and the effective capacity of the resin. The quantity of feedwater softened is plotted against the raw feedwater TDS for the four levels of regenerant brine TDS on Figure 7. The plot indicates that the quantity of water softened after regeneration with a given TDS brine decreases with increasing feedwater TDS. This is largely because the Ca content in the feedwater (and the amount removed) varies directly with the raw feedwater TDS.

TABLE 3

SUMMARY OF TYPICAL PERFORMANCE DATA
ION-EXCHANGE TEST RUNS

Number of Runs	Regenerant Brine TDS (mg/L)	Date (1977)	New Regenerant Brine TDS (mg/L)	Raw Feedwater			Softened Feedwater		Ca Removed (percent)	Resin Effective Capacity (percent)
				TDS (mg/L)		Ca (mg/L)	Volume (gal) (L)	Ca (mg/L)		
				High	Low					
27	70 000	4-20	75 000	6 000	--	390	37.5	9	97.7	31.25
							142			
		6-01	72 000	--	4 400	375	40	9	97.6	32.02
							152			
39	60 000	6-30	59 000	4 850	--	392	38	9	97.7	31.84
							144			
		8-22	60 000	--	3 800	304	49	6	98.0	31.94
							186			
43	50 000	11-04	50 000	3 850	--	304	38	8	97.4	24.60
							144			
		9-20	50 000	--	2 650	216	62	5	97.7	28.62
							235			
25	45 000	12-28	46 000	4 400	--	368	29	12	96.7	22.58
							110			
		12-07	45 500	--	3 650	304	42	10	96.7	27.19
							159			

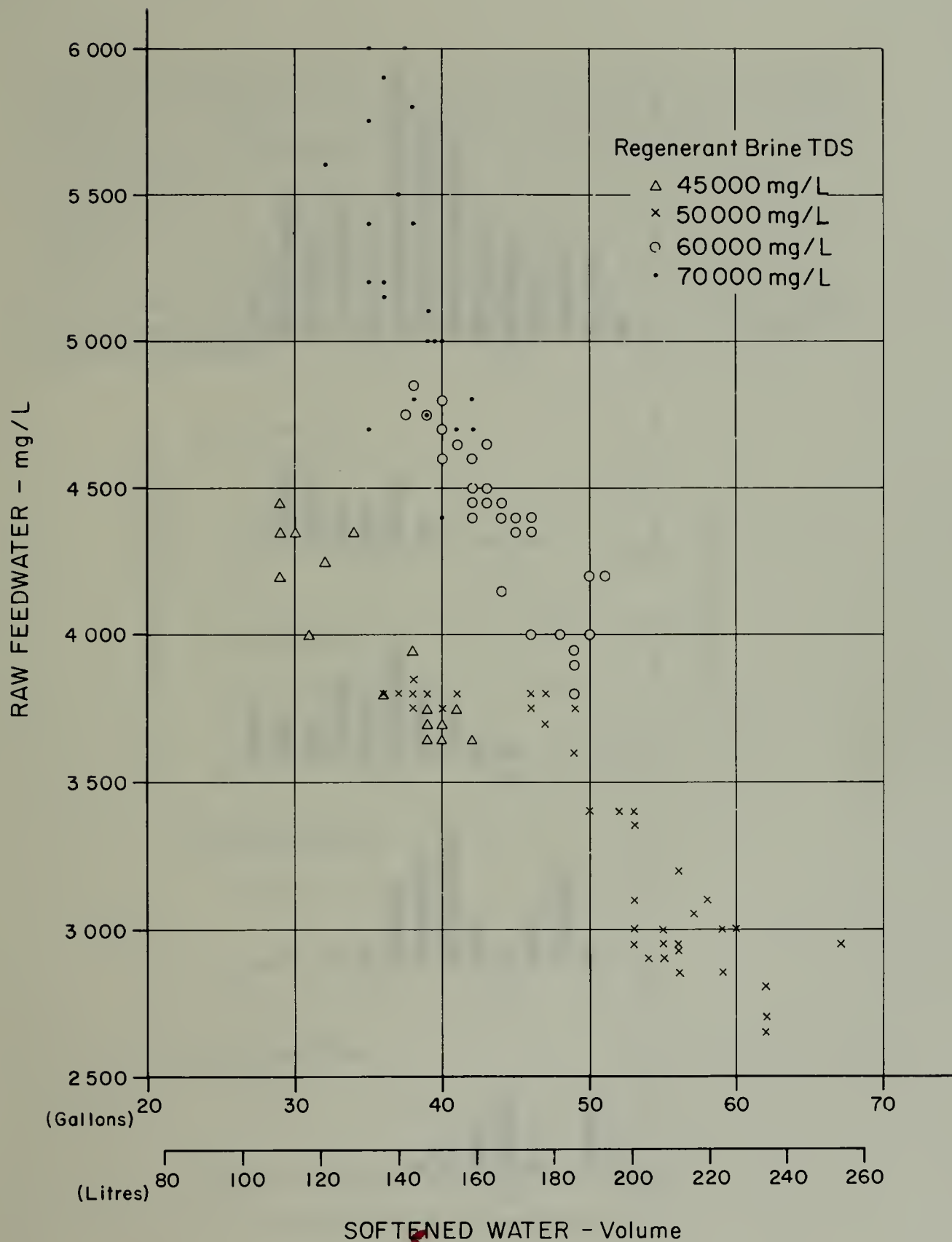


Figure 7. Feedwater Softened at Various Regenerant Brine TDS

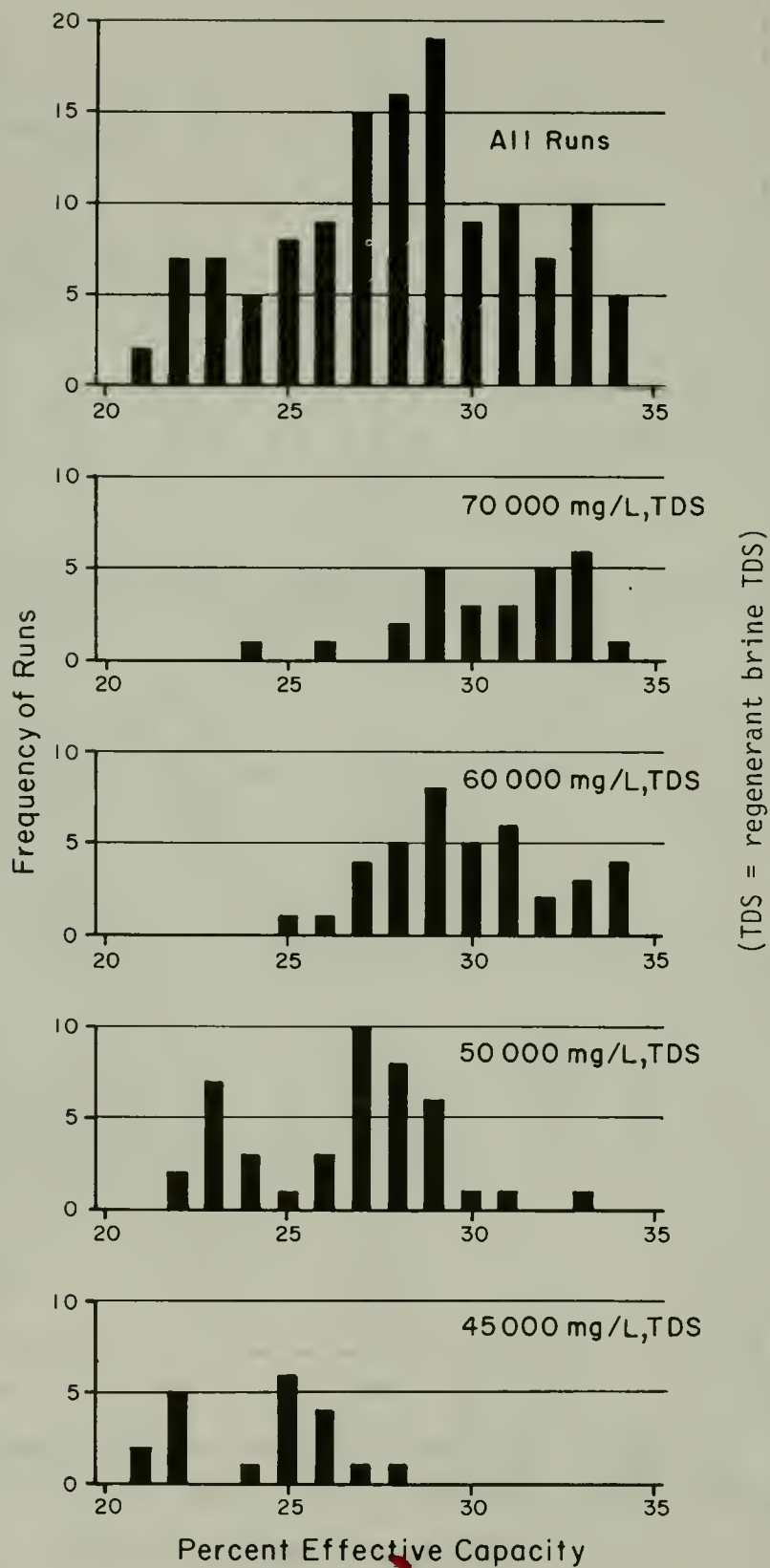


Figure 8. Effective Capacity of Ion-Exchange Resin

The percent effective capacity of the resin calculated for the completed cycles and the frequencies of occurrence for the four series are shown in percentages on Figure 8. The effective capacity was based on a ratio of quantity of Ca removed from the feedwater to the total exchange capacity of 2.1 equivalents of calcium carbonate (CaCO_3) per litre of resin (45.8 kilograins of CaCO_3 per cubic foot of resin). Since the resin also removed the hardness constituent, Mg, its exchange capacity for Ca was substantially reduced because of the large amount of Mg present in Alamitos tile drainage water. The calculated data indicated that the Ca exchange capacity of the resin improved with higher regenerant brine TDS. The modal average exchange capacity was 29 percent, and the median average capacity was 28 percent, both occurring at brine TDS between 50 000 and 60 000 mg/L.

CHAPTER VI. FUTURE STUDIES

The following is a brief description of some of the studies and projects pertaining to desalting agricultural waste water that DWR has planned for the future.

State Water Project Desalting Facility

Studies are being initiated leading to a recommendation on construction and operation of a 100 000-cubic-metre-per-day (25-million-gallon-per-day) RO desalting plant in the San Joaquin Valley to help supplement State Water Project supplies.

Softener Regeneration with Reverse-Osmosis Waste Brine

Two IX columns will be used to supply softened feedwater to an RO pilot plant. The column resin will be regenerated with RO waste brine, and tests will demonstrate on a pilot scale the ability of the RO brine/IX softening cycle to be self-sustaining.

Boron and Nitrate Removal

At the desalting demonstration plant, DWR will investigate pretreatment and/or post-treatment processes for removing boron and nitrate from the desalted water. The economic value of the product from a desalting plant can be adversely affected by the boron and nitrate content of the processed water. Treatment procedures that supplement RO membrane rejection of these potentially limiting constituents will enhance desalting plant productivity.

CHAPTER VII. FUTURE PLANNING

The preliminary investigations reviewed in this report have led to an expanded desalting study to investigate the feasibility of constructing large-scale RO desalting plants as part of the State Water Project (SWP).

The SWP, designed and built by DWR, currently supplies about 2.8 million cubic dekametres (2.2 million acre-feet) of water annually to Central and Southern California. By the year 2000, an additional 1.7 to 2.0 million dam³ (1.4 to 1.6 million ac-ft) of water per year will be required. Desalting agricultural drainage water is one possible source of additional water.

The San Joaquin Valley Interagency Drainage Program (IDP) was created in 1975 as part of a cooperative agreement among DWR, the State Water Resources Control Board, and the U. S. Bureau of Reclamation to plan for agricultural drainage and salt management. The recommended plan in the IDP final report entitled "Agricultural Drainage and Salt Management in the San Joaquin Valley", dated June 1979, calls for a valleywide drainage system to collect brackish drainage water from the west side of the San Joaquin Valley and transport it to Suisun Bay near Chipps Island.

It is estimated that by the year 2000, more than 400 000 dam³ (367,000 ac-ft) of brackish drainage water will have to be disposed of. This estimate represents drainage from approximately 210 000 hectares (520,000 acres) of land. Under an executive order of Governor Edmund G. Brown Jr., DWR is preparing a program to plan and construct brackish water desalting plants in California with a total capacity of almost 500 000 dam³ (400,000 ac-ft) per year by 2000.

Planning Study

When the IDP completed its final report, the estimated cost of desalting agricultural drainage water was about \$240 per dam³ (\$300 per ac-ft). At the same time, planning studies indicated that some proposed water projects in California would have marginal water costs approximating the cost of desalting brackish water. Based upon this cost comparison and its previous pilot-plant research on desalting and other methods of treating agricultural drainage water, DWR believes that desalting deserves closer study to determine whether it would be a cost-effective alternative water supply for the SWP.

The first phase of this two-phase planning study was a reconnaissance-level investigation to determine the questions that must be answered, the field work needed to provide the answers, the approximate costs, and the conceptual design of the prototype SWP desalting facility. This phase of the program is now complete.

The second phase of the planning study is now underway. The objectives of this phase are to (1) determine the feasibility of brackish agricultural drainage water desalting plants for the SWP, (2) develop plans and designs

for such facilities, and (3) make recommendations on the establishment and operation of desalting plants as part of the SWP.

The main feature of the phase will be the design, construction, operation, and evaluation of a large-scale demonstration desalting facility that will be used to develop data to prepare preliminary designs and cost estimates for a prototype SWP desalting plant. The site of this facility is in the City of Los Banos adjacent to the San Luis Drain, from which feedwater will be pumped.

Plans and specifications for the demonstration facility were completed in November 1981. Initial operation is scheduled to begin in early 1983, before the facility is fully constructed. Completion of construction is scheduled for May 1983, and completion of operation is scheduled for June 1985.

When these phases of the study are complete, assuming that the commercial feasibility of the desalting alternative has been established, DWR will prepare detailed plans and specifications for a prototype desalting plant with an approximate capacity of 95 megalitres (25 million gallons) per day. Up to 370 000 dam³ (300,000 ac-ft) per year of agricultural drainage water may eventually be desalted in the San Joaquin Valley, with an additional 125 000 dam³ (100,000 ac-ft) per year of brackish ground water desalted in Southern California.

Technical and Cost Data

The testing at Firebaugh, described in this report and in Bulletin 196-76, has formed the basis for the design of the Los Banos Demonstration Desalting Facility. Other work on nutrient and silica removal, aquaculture, and power plant cooling has also contributed substantially to the facility's design. The basic ability of the unit treatment processes to successfully reclaim drainage water has been shown, but operating characteristics of the combined systems and their costs must still be determined. The determination of costs was not an objective of the testing described herein. However, testing at Los Banos will provide both technical data and cost data sufficient to determine the feasibility of commercial-size desalting facilities for the State Water Project.

APPENDIX

MEMBRANE FABRICATION AT THE WASTE WATER TREATMENT EVALUATION FACILITY

MEMBRANE FABRICATION AT THE WASTE WATER TREATMENT EVALUATION FACILITY^{1/}

As an adjunct to the tube-type RO plant operation, a membrane fabrication laboratory was established to equip the plant with the initial 500 tubes and to provide any replacements needed. The membranes were fabricated at the WWTEF by DWR personnel assigned to operate the RO plant.

It was decided to establish the laboratory because the manufacturing of the tubular CA membranes was determined to be a relatively simple process, requiring the use of only semiskilled labor and off-shelf supplies. This manufacturing capability made the RO operation at the WWTEF self-sufficient in membrane production and demonstrated that such manufacturing could be done on-site.

The Semipermeable Membrane

The CA membrane used in the tube-type RO plant is made by a process developed and patented by UCLA. The membrane is prepared from a solution consisting of cellulose acetate, formamide, and acetone, mixed in a typical ratio of 23:27:50 percent by weight. A viscous liquid resulting from this mixture is cast into a tubular-shaped film. The cast membrane is then fabricated into a working assembly (Figure 9) and post-treated to develop its salt-rejecting property.

The cast membrane is composed mainly of cellulose acetate and has a dense surface layer formed during the casting process and a relatively porous sublayer. The total film thickness is about 100 micrometres (3,900 microinches), and the dense layer has a thickness of about 0.2 micrometre (7.9 microinches). The thin, dense layer is formed on the side exposed to the air during casting and is the primary barrier to salt passage. This surface must be in contact with the brine to gain full membrane performance.

As a final step in fabrication, the membrane is cured by immersion in a hot-water bath. An uncured membrane offers virtually no resistance to salt passage. The curing process gives the membrane its salt-rejecting property. Cure temperatures range from 76 to 94° C (169 to 201° F) with permeability to both water and salt decreasing with increasing cure temperature. Thus, a membrane cured at 76° C (169° F) has a high permeability and is referred to as a "loose" membrane, while one cured at 94° C (201° F) has a low permeability and is considered a "tight" membrane.

^{1/} California Department of Water Resources, San Joaquin District, "Agricultural Waste Water Desalination Report No. 13", February 3, 1977 (revised).

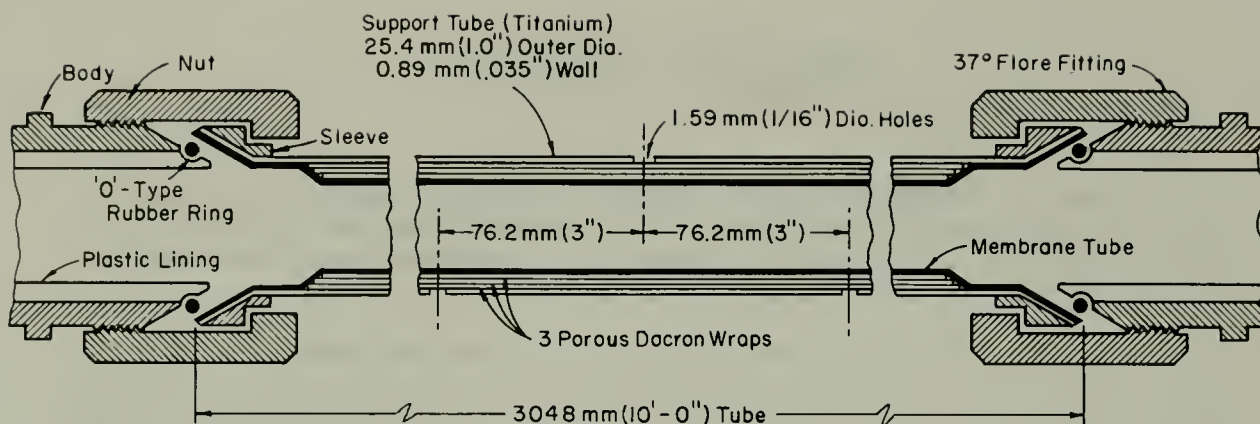


Figure 9. Typical Tubular Assembly – 500-Tube (UCLA) RO Unit

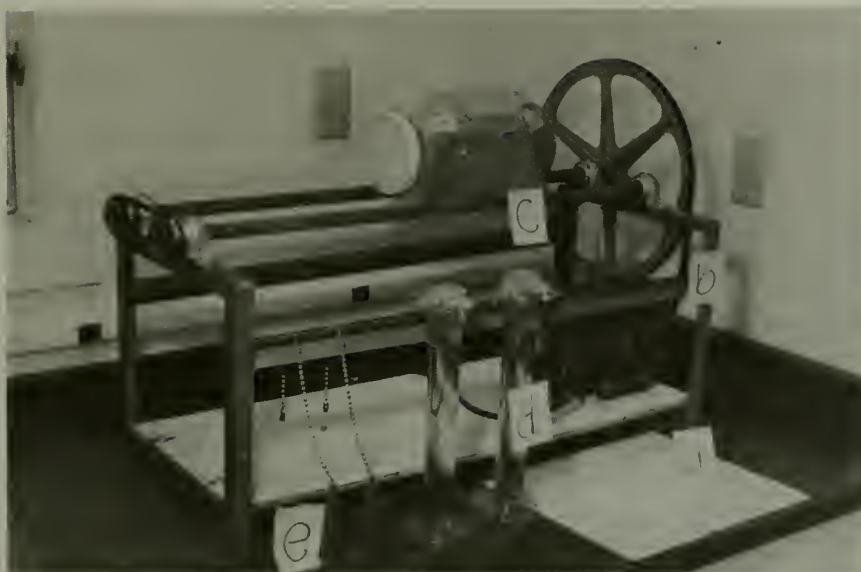
Membrane Fabrication Operation

The membrane fabrication equipment and procedure were adapted from the method developed by UCLA. The UCLA engineering staff trained DWR personnel in membrane fabrication at UCLA, helped establish the fabrication operation at the WTEF, and reviewed the operation during the early stages. Many of the special tools and equipment used for fabricating the membrane were provided by UCLA.

The cellulose acetate used for making the CA membrane is supplied in powder form by the Eastman Company under the designation CA400-25. This powder is first dissolved in acetone, formamide is then added, and the chemicals are mixed on a roller-mixer for 24 hours. The solution is then transferred to a 250-millilitre (0.066-gallon) cylinder in the amount required to charge one casting operation (Figure 10).

The membrane is batch-cast using a specially designed apparatus (Figure 11). A casting tube is used to form the membrane into a tubular shape. The bottom of the tube is charged with casting solution, and a casting bob is inserted to hold the solution in place (Figure 12). A winch-driven chain is used to pull the bob upward through the tube at a rate of about 0.15 metre (6 inches) per second. The bob pushes the casting solution ahead of it, leaving a thin film of solution on the inner wall of the tube.

The casting tube is immediately dropped into chilled water located below the casting apparatus. The water is held at a temperature of 1° C (34° F) to gel the solution. The casting tube is then transferred to a shrink tank containing hot water at 80° C (176° F). The shrinking process allows the membrane to be removed from the casting tube (Figure 13).



- a - cellulose acetate powder
- b - roller-mixer
- c - solution in 1-gallon container
- d - solution in 250-millilitre cylinder
- e - casting bob



Container of cellulose acetate, formamide, and acetone solution being rolled on a roller-mixer.

FIGURE 10. EQUIPMENT FOR PREPARING MEMBRANE CASTING SOLUTION

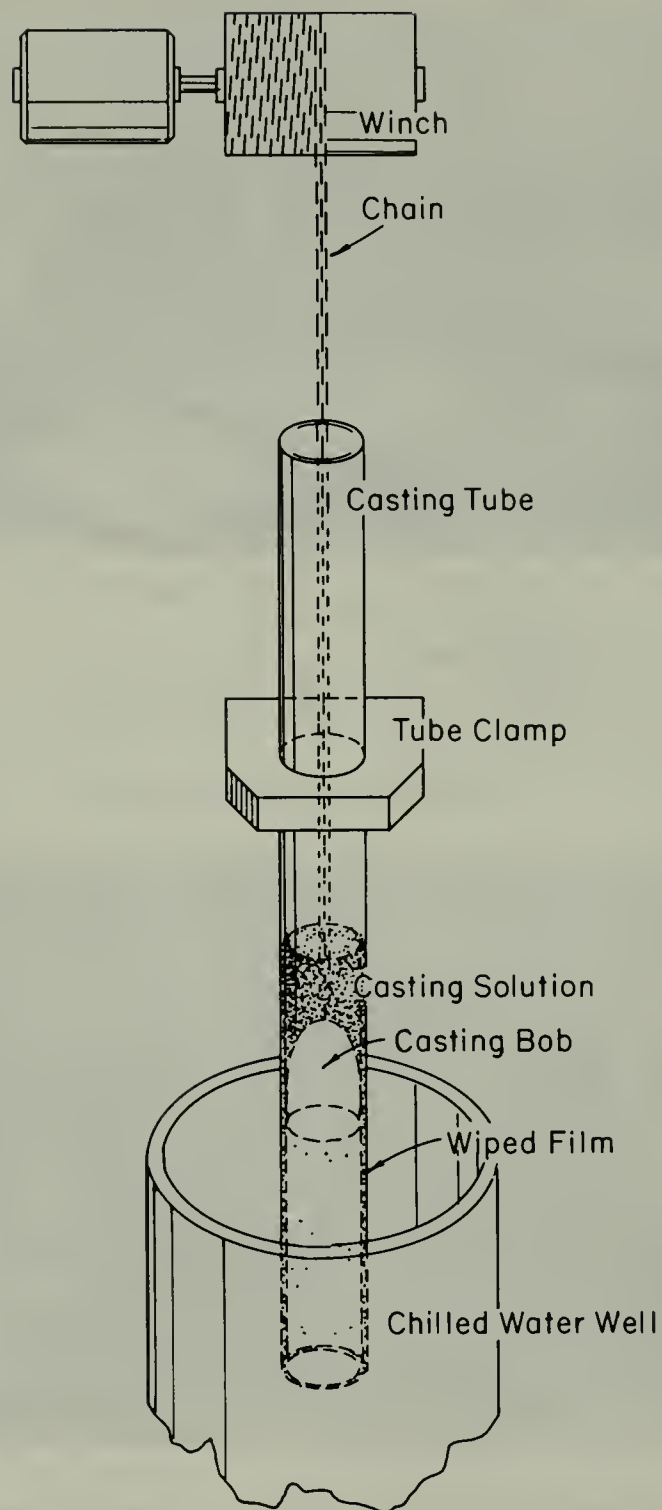
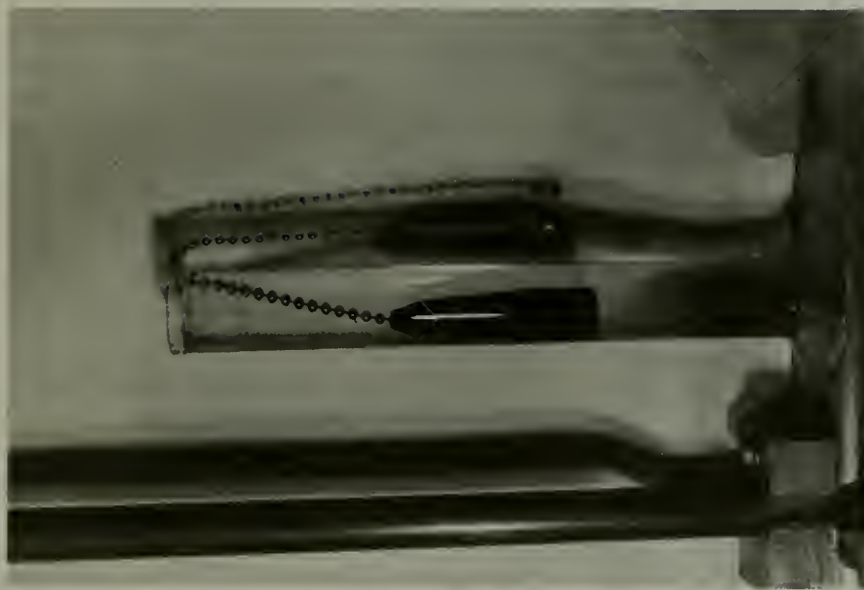


Figure II. RO Membrane Casting Apparatus



Bottom of tube is filled with solution; bob holds solution in place.



Casting bob is placed in cylinder containing solution.

FIGURE 12. CHARGING CASTING TUBE WITH MEMBRANE SOLUTION



Pulling membrane from casting tube
after shrinking in hot water tank.



- a - membrane shrink tank
- b - membrane pulled from casting tube
- c - dacron cloth, 203 by 3050 millimetres

FIGURE 13. REMOVING MEMBRANE FROM CASTING TUBE

After removal from the casting tube, the membrane is wrapped in three layers of dacron cloth and inserted in a titanium support tube (Figures 14 and 15). The ends of the membrane are trimmed, plastic-coated, and flared to conform to the flared tube connector (Figure 16).

The completed assembly (Figure 9) is installed in a curing loop through which hot water at a pH of 4.5 is circulated for 15 minutes (Figures 17 and 18). The loop is then flushed with cold water at a pH of about 7.1.

The water heater and pump supply water at a nominal temperature of 90° C (194° F) and a pressure of 69 kPa (10 psi), respectively. Citric acid is added to the water to maintain a pH of 4.5. There is a slight variation in the cure temperature because of heat loss in the curing loop. This curing process develops the membrane's salt-rejecting property, and a water temperature of 90° C (194° F) gives the membrane an intermediate permeability to both water flux and salt.

As a final step, the tube assemblies are installed on the test rack where they are proof-tested for defects and desalting performance (Figures 19 and 20). Feedwater containing NaCl solution at a concentration of 5 000 mg/L is passed through the test rack at a flow rate of 0.32 L/sec (5 gpm) and 2 800-kPa (400-psi) pressure. Table 4 shows the results of a typical two-day test run.

The tube assemblies are usually used immediately following testing. Any tube held in storage is filled with water because the CA membrane must always be wet to prevent deterioration. The small amount of Roccal disinfectant is added to the water to retard bacterial growth.

Field personnel at the WWTEF successfully fabricated all tube assemblies for the 500-tube RO plant and supplied all replacements. Approximately 15 to 20 complete tubes were fabricated in a single day. Considerable care was exercised during preparation of the membranes to avoid physical damage such as scratching, crimping, or stretching. Membrane rejection amounted to about 10 percent of a day's production and was mostly the result of surface flaws or inadequate shrinkage.



Membrane ready for rolling.



Rolling membrane in three wraps of dacron cloth.

FIGURE 14. ROLLING MEMBRANE IN DACRON CLOTH



Ready to insert membrane in support tube.



Support tube is pulled over membrane
and three wraps of dacron cloth.

FIGURE 15. INSERTING MEMBRANE IN TITANIUM SUPPORT TUBE



End of membrane is trimmed, plastic-coated, and flared.



End of membrane alongside flared tube connector.



Two types of tube connectors (note plastic lining in connector on right).

FIGURE 16. END OF MEMBRANE IS PREPARED FOR TUBE CONNECTOR

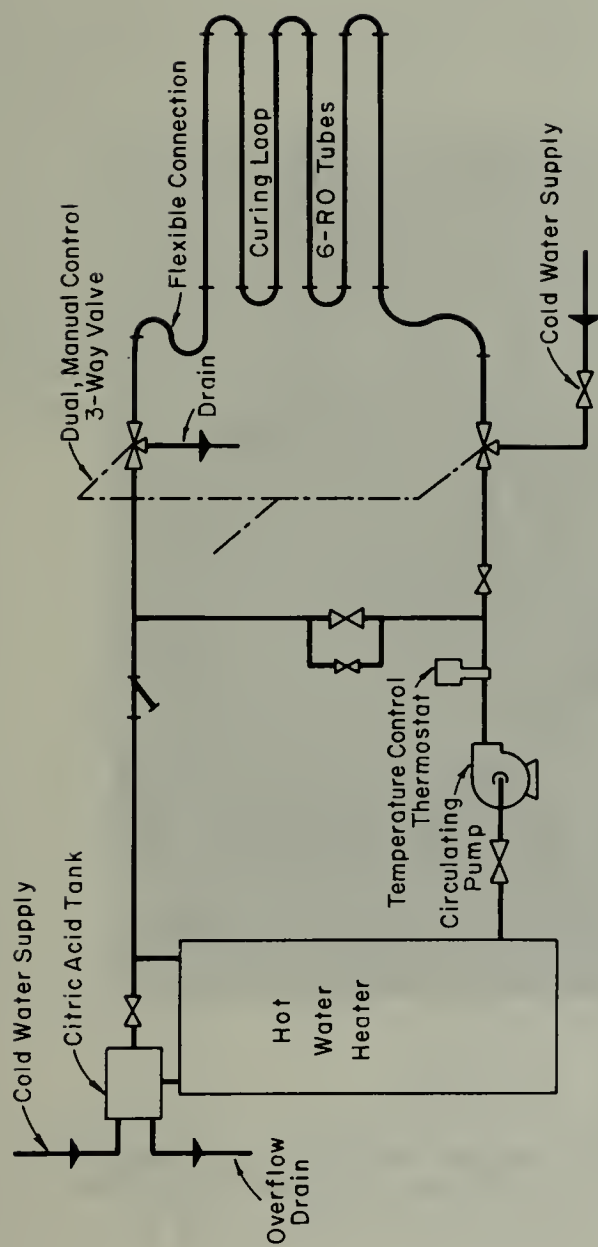


Figure 17. RO Membrane Curing Loop



FIGURE 18. REVERSE-OSMOSIS TUBE ASSEMBLIES
IN CURING LOOP ABOVE CURE TANK

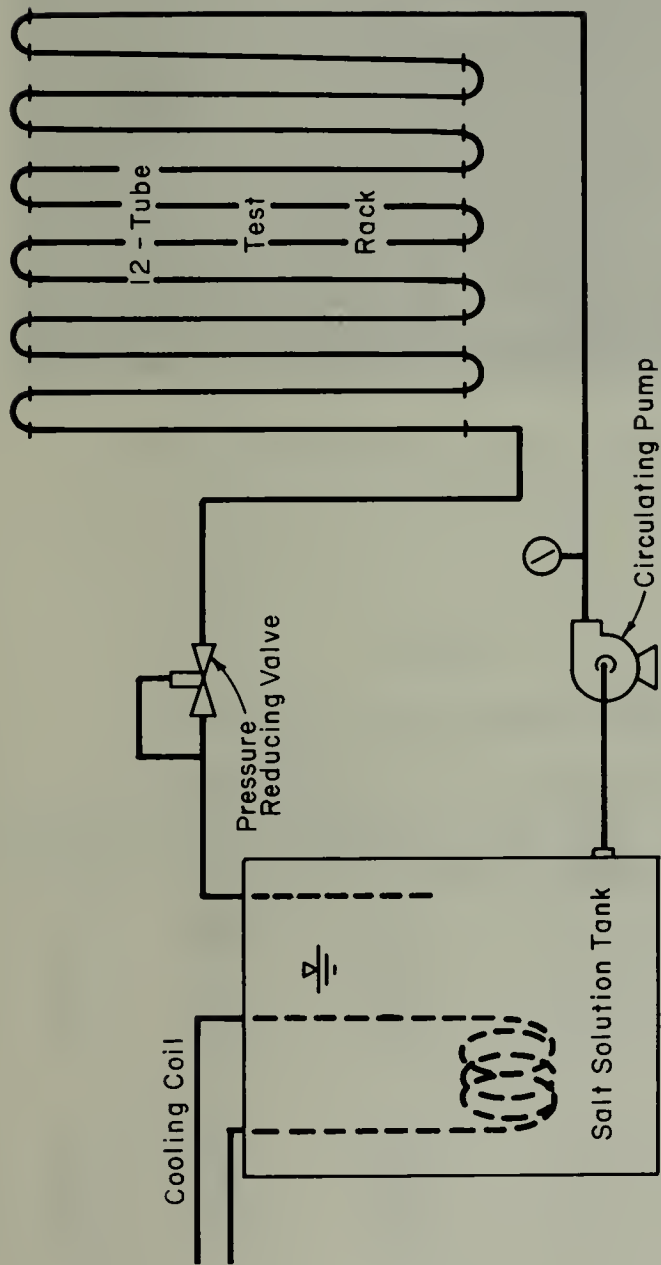


Figure 19. RO Tubular Assembly – Test Unit

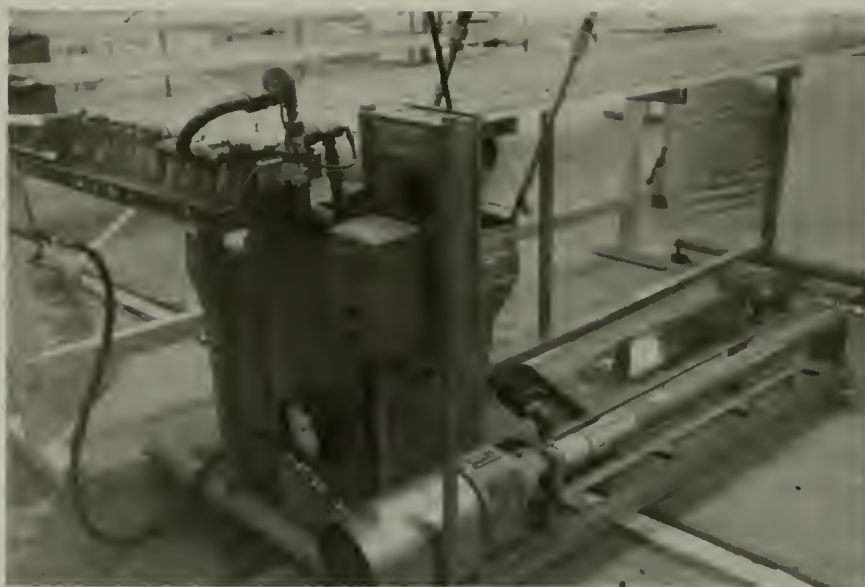


FIGURE 20. TUBULAR ASSEMBLY TEST UNIT

TABLE 4
REVERSE-OSMOSIS TUBE TEST RESULTS

Date	Feedwater NaCl (mg/L)	Test Slot Number	Product Water			DR ^{3/}
			Flux		NaCl (mg/L)	
			(mm ³ /min) ^{1/}	(gfd) ^{2/}		
3-12-76	4 800	1	840	14.3	310	15.48
		2	850	14.4	270	17.78
		3	840	14.3	380	16.84
		4	920	15.6	345	12.63
		5	930	16.0	380	13.91
3-16-76	5 200	1	1 170	19.9	470	11.06
		2	1 150	19.6	410	12.68
		3	1 150	19.6	460	11.30
		4	1 220	20.7	490	10.61
		5	1 220	20.7	410	12.68

^{1/} Cubic millimetres per minute (per tube).

^{2/} Gallons per square foot per day (of membrane area).

^{3/} Desalination ratio = salt concentration of feedwater ÷
salt concentration of product water.

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